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(71) Applicant: International Business Machines Corporation
Old Orchard Road
Armonk, N.Y. 10504(US)

(72) Inventor: Pennington, Keith Samuel
Londonderry Lane
Somers New York, 10589(US)
Inventor: Cohen, Mitchell Simmons
23 Gregory Lane
Ossining New York 10562(US)
Inventor: Sachdev, Krishna Gandhi
14 Tanglewood Drive
Wappingers Falls New York 12590(US)

(74) Representative: Atchley, Martin John Waldegrave
IBM United Kingdom Limited Intellectual Property Department Hursley Park
Winchester Hampshire SO21 2JN(GB)

(54) Recording medium for recording apparatus such as printing apparatus.

(57) The present invention relates to a recording medium (10) for use in a recording apparatus comprising a substrate (12), a sensitive layer (16) and an electrically conducting layer (14).

The invention is characterised in that the sensitive layer (16) is formed from a material which is hydrophilic at temperatures below about 150 degrees C and is capable of having its hydrophilicity locally reduced by the passage of electrical current therethrough.

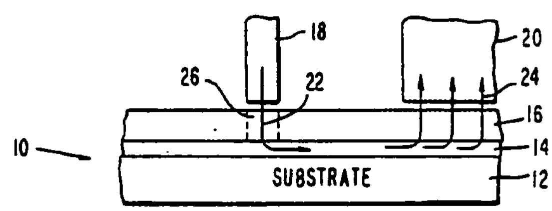

FIG.1

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RECORDING MEDIUM FOR RECORDING APPARATUS SUCH AS PRINTING APPARATUS

Th present invention relates to a recording medium for use in a recording apparatus, for example a printing apparatus, and in particular to the production of offset masters and negatives for use in printing processes.

Both resistive ribbon thermal transfer printing and electroerosion printing are known in the art for providing high resolution, good quality printing, especially of the type that is used in computer terminals and typewriters.

Resistive ribbon thermal transfer printing is a type of thermal transfer printing in which a thin ribbon is used. The ribbon generally comprises either three or four layers, including a support layer, a layer of fusible ink that is brought into contact with the receiving medium (such as paper), and a layer of electrically resistive material. In a variation, the resistive layer is thick enough to be the support layer, so that a separate support layer is not needed. A thin, electrically conductive layer is also optionally provided to serve as a current return.

In order to transfer ink from the fusible ink layer to the receiving medium, the layer of ink is brought into contact with the receiving surface. The ribbon is also contacted by an electrical power supply and selectively contacted by a thin printing stylus at those points opposite the receiving medium where it is desired to print. When current is applied via the thin printing stylus, it travels through the resistive layer and causes localised resistive heating, which in turn melts a small volume of ink in the fusible ink layer. This melted ink is then transferred to the receiving medium to produce printing. Resistive ribbon thermal transfer printing is described by way of example in US-A-3,744,611; A-4,309,117; A-4,400,100; A-4,491,431 and A-4,491,432.

The materials used in ribbons for resistive ribbon thermal transfer printing are well known in the art. For example, the resistive layer is commonly a carbon or graphite-filled polymer, such as polycarbonate. The thin current return layer is a metal, such as Al. The thermally fusible inks are various resins having a colourant therein, and typically melt at about 100 degrees C. Printing currents of approximately 20-30 mA are used in the present, commercially available printers.

Electroerosion printing is also well known in the art, and is described by way of example in US-A-3,786,518; A-3,861,952; A-4,339,758 and A-4,086,853. Electroerosion printing is known as a techniqu which is suitable to make direct offset masters and direct negatives. Generally, the electroerosion recording medium comprises a support layer and a thin electrically conductive layer. The support layer can be, for example, paper, polyesters such as Mylar (Registered Trade Mark), etc., while the thin conductive layer is a metal, such as Al. In order to produce a recording medium which can be used in a printing process, portions of the thin Al layer are removed by an electric arc. To do so, a printing head comprising multiple styli, typically tungsten wire styli of diameters 0.3-0.5 mil - (0.3 -0.5 $\times$ 10^{-3} inch), is swept across th electroerosion medium while maintaining good electrical contact between the styli tips and the aluminium layer. When an area of the medium is to be prepared for a printing operation, a pulse is applied to the appropriate stylus at the correct time, resulting in an arc between the energised stylus and the aluminium layer. This arc is hot enough to cause local removal of the aluminium by disintegration, e.g., vaporisation.

Practical electroerosion media require a base layer between the supporting substrate and the thin metal layer, as well as an overlay layer on the thin metal layer. The base layer and the overlay layer are used to prevent scratching the aluminium layer in areas where no arc is applied, and to minimise head wear and fouling. Typically, the base layer is a hard layer consisting of hard particles embedded in a suitable binder, such as silica in a cross-linked cellulosic binder. The overlay layer is typically a lubricating, protective overlayer comprising of a polymer including a solid lubricant, such as graphite in a cellulosic binder.

Depending upon the properties of the various layers in the recording medium produced by the electroerosion process, a direct negative or a direct offset master can be formed.

For example, a direct negative can be formed from a transparent polymer support layer and a thin aluminium layer directly deposited on the support layer. After the electroerosion writing process, the Al layer is patterned with holes. Since the Al layer is reflective to light while the supporting substrate is transparent, the electroerosion writing process has produced the required light opaque and light transparent regions needed to make a negative. The electroeroded negative can be used in a plate-making machine of the type used to make a "master," such as that used in offset photolithography. The master would be made by contact printing using the electroeroded negative.

Alternatively, a direct mast r can be easily made by the electroerosion process in order t simplify the operation by which masters, or plates, are made in conventional offset lithography shops. In such an operation, the electroerosion medium typically comprises the support layer, a base layer which is hydrophobic, an Al layer, and an optional overlay layer. When the Al layer has been written on by being electroeroded and the overlay layer has been removed, regions of the Al layer - (unwritten areas) and the base layer (written eroded areas) will be exposed. Since the Al layer is hydrophilic, the unwritten areas having Al will attract water but will repel organic inks. The written areas of the recording medium, being formed by the hydrophobic base layer, will repel water but will accept organic based inks. A direct master is thereby produced, since the information to be printed has been successfully mapped onto the master in terms of surface affinity to water and ink.

If the problem of scratching of the Al layer in undesired areas were not present, the substrate-Al layer combination could itself be used for direct negative and direct master applications. For a direct negative, a clear hydrophobic polymer sheet, typically polyester, can be used as the substrate. Since this is transparent to light while the Al is reflective, a direct negative would be obtained. Also, since the Al is hydrophilic and the polyester substrate is hydrophobic, a direct master would also be created in principle.

Heretofore, electroerosion has been used to provide lithographic printing masters, but the lifetimes of these masters in actual use is not as extensive as when the traditional printing plates, or masters, are made using various chemical treatments to prepare a photosensitised plate. One technique for producing offset masters directly is that described in US-A-4,081,572 where a light beam from a laser is used to change selected regions of a hydrophilic polymer layer to a hydrophobic state, thereby creating ink receptive and ink repelling regions. However, such a technique is not as directly usable in standard commercial processes, is expensive, and generally consumes more power. Since a considerable amount of power is required to operate the laser, the overall energy efficiency of this type of system is very low. Also, the system requires an additional, high quality optical system to concentrate and direct the light beam, or a mask which must be aligned in order to define the portions of the polymer layer which are to be exposed to the light beam.

Printing techniqu s, such as facsimile printing, often incorporat dyes whose c lour can be changed in localities where a discharge of current occurs. An example of this is described in US-A-3,113,512, wherein electrically-induced colour changes in a sheet are grouped so as to reproduce the original image scanned by a sending device.

Generally, the prior art has not provided a technique for creating offset masters or direct negatives using equipment which is energy efficient and suitable for processing using commercially available apparatus. Still further, colour changes of the types known in the art using dyes and electrochromic materials do not provide sheets which are very stable over the range of all normal environmental variations of either temperature or light. In the prior art, it has been desired to provide writing with as low a current as possible and at as high a speed as possible, and for these reasons many of the chemical changes which were used for printing were those types of chemical changes which would occur at low temperatures (typically 100 degrees C, or less). However, the use of such materials is disadvantageous, since ambient conditions are often such that very high temperatures and/or light (such as ultraviolet light) are present, which will cause gradual colour changes in the sheets.

It is also desirable to provide a system in which the necessary energy for producing a localised change can be economically provided and delivered in a very efficient manner to the recording medium in which the change is to be made. This will reduce the overall power requirements and make the system more readily applicable for commercial applications. Still further, it would be advantageous if a system could be provided which would have the resolution and print quality equal to or better than that associated with commercial technologies, such as resistive ribbon printing and electroerosion printing. The techniques of the prior art do not provide inherent stability against effects of the environment, and do not extend the capabilities of either resistive ribbon printing or electroerosion printing, which are two very efficient printing technologies especially suitable for computer output terminals and typewriter-like operations.

The object of the present invention is to provide an improved recording medium for use in a recording apparatus, for example a printing apparatus.

The present invention relates to a recording medium for use in a recording apparatus comprising a substrate, a sensitive layer and an electrically conducting layer.

The invention is characterised in that the sensitive layer is formed from a material which is hydrophilic at temperatures below about 150 degrees C and is capable of having its hydrophilicity locally reduced by the passage of electrical current therethrough.

According to one embodiment of the invention, a multi-stylus printing head, of the type used in resistive ribbon printing or electroerosion printing, is used to provide localised currents in a resistive layer of a recording medium. The recording medium comprises the resistive layer, a thin conductive layer such as metal, and a supporting substrate. If the thin conductive layer is to be transparent InSnO can be used, together with a substrate which is also light transparent. The regions of the resistive layer through which high density electrical currents pass from the recording styli undergo chemical changes, changing the ink-retention properties and/or colour of these regions. For example, a hydrophilic resistive layer can be converted to a hydrophobic state in localised areas by resistive heating due to the passage of electrical current of high density therethrough, which will make these regions ink attractive (oleophilic). The remaining portions of the resistive layer will retain their hydrophilic character, so that regions of ink retention and repulsion will be formed. This provides a master for use in a printing process.

The resistive layer is typically a polymer layer which can be made to have a resistivity similar in magnitude to the resitivity found in the resistive layers of resistive printing ribbons. The thickness of the resistive layer depends upon the life desired for the master and on the resolution to be obtained. Typically the resistive layer is about 0.5-2 mils (0.5 -2 $\times$ 10^{-3} inch) in thickness. If the recording medium is to be used only for printing, rather than as a printing master, the thickness of the resistive layer can be made much less, for example, 5 microns and less.

With this technique, the attainable resolution depends upon the recording styli diameter and the thickness of the resistive layer. Resolution and printing quality equivalent to or better than that of resistive ribbon printing and electroerosion printing are readily available using this technique. Additionally, the current and power requirements will be less than those in conventional resistive ribbon printing, and will be typically 14-20 mA, at 10-12 V.

In order that the invention may be more readily understood an embodiment will now be described with reference to the accompanying drawings, in which:

Figure 1 shows a printing apparatus utilising a recording medium in accordanc with the invention and in which electrical current from a printing stylus passes through a resistive layer on th recording medium and causes a change in the colour and/or ink retention properties of the layer,

Figure 2 schematically illustrates another apparatus utilising a recording medium in accordance with the invention in which both an interior conductive layer and a substrate layer in the recording medium are transparent, and a resistive layer in the recording medium, through which current passes, undergoes colour changes to effect a printing operation,

Figures 3, 4, 5, 6 and 7 illustrate chemical transformations which take place in different materials selected for a recording medium in accordance with the invention.

The printing apparatus to be described uses high density electrical currents to produce intense resistive heating to locally change the chemical behaviour of a resistive layer in a recording medium. In this manner, the ink retention properties and/or colour of the resistive layer can be locally changed so that the resistive layer can be used for printing and for the production of negatives and masters, without requiring wet chemical processing, electroerosion of a thin metal layer, or the necessity for a fusible ink layer.

In the apparatus illustrated in Figure 1, a recording medium 10 comprises a substrate or support layer 12, a thin electrically conductive layer 14, and a resistive layer 16. In order to direct electrical currents into the resistive layer 16, a multi-stylus head of the type used in either resistive ribbon printing or electroerosion printing is provided. This type of head is well known in the art and comprises a plurality of printing styli (one of which is shown at 18) and a large contact (ground) electrode 20. When a selected pattern of printing styli 18 is energized, electrical currents, represented by the arrows 22 will flow from the styli and through the resistive layer 16 and will return to the ground electrode 20 via the conductive layer 14, as represented by arrows 24. If the current density is sufficiently high in the region of the resistive layer 16 in the vicinity of the printing stylus 18, intense resistive heating will occur and a small region 26 of the resistive layer 16 will have its properties and/or colour changed. In particular, if the resistive layer 16 is initially hydrophilic, region 26 can be made oleophilic by the passage of high density electrical current therethrough.

The apparatus of Figure 1 is v ry similar to that used in resistive ribbon printing, except that the fusible ink layer is missing. The resistive layer 16 has a resistivity similar to that of the resistive layers in resistive printing ribbons, typically from about 200 to 1,200 ohms/square. The thickness of the resistive layer 16 depends upon the required printing resolution and plate life of the recording medium 10, when it is used as a master. For printing uses where the ink retention properties of the resistive layer do not have to be changed, i.e. where it is not to be used as a master, the resistive layer can be less than 5 microns thick. When the recording medium 10 has its ink retention properties changed and is to be used as a plate in offset lithography, the thickness of layer 16 is generally about 0.2-2 mils (0.2 -2 $\times$ 10^{-3} inch).

The conductive layer 14 is formed from any type of metal, including Al, Ni, Cr, Cu, stainless steel, etc. Its thickness is generally about 1,000 angstroms.

The substrate or support layer 12 can be any of the generally used materials, including Mylar - (Registered Trade Mark) (polyethylene teraphthalate), Teflon (Registered Trade Mark) (polytetrafluoroethylene), polyesters, etc. Its thickness is usually about 1 micron.

The resistive layer 16 is formed from a polymer having limited conductivity, and is initially hydrophilic. When the temperature of the polymer is locally raised to a sufficient value in excess of about 150 degrees C, it will undergo a chemical change and will be converted to a hydrophobic material. Resistive polymers suitable for use as layer 16 are those which will undergo no chemical or physical changes at temperatures below approximately 150 degrees C. Preferably, no chemical changes will occur until the temperatures are in excess of 250 degrees C, and usually in the range 300-400 degrees C. This means that these materials will be very stable under ordinary ambient conditions, and will experience no colour changes and/or structural or chemical changes even upon storage in hostile environments for long periods of time.

One class of suitable resistive materials for layer 16 is a polymer binder having electrically conductive materials therein, such as ZnO, TiO_2, CdS or graphite. A built-in mechanism for visible change can also be included in the resistive layer. The binder has structural features that allow thermally-induced dehydration and reduced hydrophilicity in the image areas when an electrical current pulse is applied to these areas.

An example of a suitable polymeric binder is polyamic acid which, upon the application of an electrical pulse, will undergo thermal ring closure to a polyimide precursor.

While the polyamic acid is hydrophilic, the polyimide precursor is hydrophobic. This transformation is depicted in Figure 3.

Other polymer systems with thermally labile pendant groups on the polymer chain can also be used for image formation when high density electrical currents are passed through the resistive layer 16.

The resistive layer 16 can be formed as a coating applied to the thin metal layer 14 from polar solvents such as diglyme, glyme, THF - (tetrahydrofuran), or NMP (n-metal pyrrodlidone). The coatings are then dried at about 100 degrees C.

Polyamic acid films have enhanced wear resistance and a low coefficient of friction which can be further improved by incorporating a silicon moiety. Such siloxane modified polyamic acids are known, and are commercially available from M and T Corporation. If desired, a visible change can be produced when the electrical current pulse is applied by incorporating a colour formation material which will undergo a colour change only at these elevated temperatures. These dyes are well known in imaging methods and processes, and typically are very stable at temperatures below about 150 degrees C.

Other classes of materials can be used for the resistive layer 16, in order to provide direct image formation upon the application of electrical current pulses. As noted, these can be used to make long run printing offset masters. One such class of resistive polymers comprises ionic polymers which are hydrophilic and exhibit good wear resistance. Conductive fillers, such as ZnO, CdS, ZnI_2, MoO, etc, are added to modulate the conductivity and water-holding capacity of these ionic polymers. Additionally, dye forming systems can be incorporated including either Leuco or thermochromic dyes. The use of these dyes will provide a visible change in the electrically imaged areas.

When writing is effected by computer actuated electrical pulses applied to the recording head, the electrical currents will cause the hydrophilic ionic polymer to undergo a cross-linking reaction that results in the loss of ionic character in the imaged area.The written areas will now become oleophilic, while the unwritten areas will remain hydrophilic. Thus, the recording medium 10 can be used directly as an offset master or as a photonegative.

An xample of an ionic polymer which can be converted into a non-ionic polymer by the application of electrical energy is a polyacrylic acid-polyamine complex, which is hydrophilic and ionic. The transformation of this material to an oleophilic state when electrical energy is applied is represented by the diagram in Figure 4.

This concept is also adaptable to work in polymer-metal mapping for written-unwritten areas, respectively. Thus, if the ionic polymer system is soluble in water/alcohol solvents, the unwritten areas can be removed with the solvents while the written areas remain intact because they have been made insoluble by the application of electrical energy during the writing operation.

Another class of suitable materials for the resistive layer 16 includes those materials which are thermally cross-linkable and water insoluble. Materials of this class can be used to provide masters having long press life for printing thousands of copies. The resistive layer 16 includes a hydrophilic, water insoluble polymer binder and conductive material such as NnO, TiO_2, MoO, CdS, Sb_2O_3, ZnI_2, graphite, etc. The thermally cross-linkable binder is one which will change from a hydrophilic state to a hydrophobic state when electrical currents of sufficiently high density are applied to the resistive layer 16 from the printing stylus 18. The non-imaged areas (where no electrical current is applied) of the resistive layer 16 remain hydrophilic. If desired, a visual change can also be produced by incorporating a thermochromic dye in the resistive layer.

Suitable polymers for the thermally cross-linkable binder include combinations of low molecular weight Novolak type resins (orphenolformaldehyde-type) and polyacrylamides. When electrical energy is applied to this material, the Novolak resins are transformed to highly cross-linked resols, and acrylamide will change to a less basic imide or nitride. The end result is that the electrically imaged area of the resistive layer will be made hydrophobic, while the remainder of the resitive layer will stay hydrophilic. An example of this transformation is shown in Figure 5.

Polyacrylamides in this combination can be replaced by high molecular weight polyamines, polyethers, polyoxyethylene aryl ether, polyvinyl pyrrolidone, etc.

Polyvinyl acetal resins with thermo-setting resins such as phenolics, epoxies, ureas, melamines, and di-isocyanates can also be employed.

Poly functional monomers, such as pentacrythritai triacrylate can be included as an additive in polyvinyl alcohol, polyacrylamide, or polyacrylates to cause thermally-induced, cross-linking of the written area.

In addition to these materials, diazopolyacrylamides can be used, since they are hydrophilic polymers that are ionic. Upon heating, the loss of the diazo group is accompanied by the generation of reactive intermediates which undergo cross-linking in the exposed area. An example of this transformation is indicated in Figure 6.

Other diazo and diazonium sensitizers can be employed in polymer matrices, such as phenolformaldehyde resins, PVA, polyacrylamide, and polymethylmethacrylate-methacrylic acid co-polymers. These sensitizers are used for cross-linking and hardening.

FIG. 2 shows a recording medium 28 which can be used in combination with a multi-stylus head to make projection foils. Recording medium 28 comprises a transparent substrate 30, such as Mylar (Registered Trade Mark), a transparent conductive layer 31 such as InSnO, and a resistiv layer 32 in which colour can be produced for a colour change brought about by the passage of electrical current through the layer. For this purpose, a multi-stylus head includes printing electrodes or styli (one of which is shown at 34) and a broad contact (ground) electrode 36. High density localized current flow beneath the printing stylus 34 is indicated by arrow 38, while arrows 40 indicate the lower density return current flow through ground electrode 36. The high density localized current beneath the printing stylus 34 changes the colour of region 42 in order to make the coloured foil.

The resistive layer 32 undergoes image formation in selected areas when electric currents are localized in these areas in the layer, as a consequence of the polymer cross-linking/structure modification and/or colour formation which takes place in these areas. Resistive layer 32 is a polymer binder having conductive fillers, such as ZnO, ZnI_2, MoO, CdS, etc therein, and a colour defining material. Polymers which may be used for this application include cellulose acetate butyrate - (CAB), CAB-urethane, epoxies, polyimides, polyorganosiloxanes and polyether-urethane blends, polyacrylates (PMMA, glycidylmethacrylate, PMMA-MA resins), and polyvinyl alcohol-diazoacrylamides. Thermo-chromic dyes may be used for the colour formation or colour change, as indicated in Figure 7.

In this type of resistive layer recording, commercially available multi-stylus printing heads can be used, of the type used in resistive ribbon printing. The recording styli may be tungsten styli having diameters of approximately 10-150 micrometers. Recording currents of approximately 0.25-25 mA can be used, depending on styli diameters, at voltages of approximately 10-12V. For example, currents of 0.25-25 mA can be used with styli having diameters of about 20 micrometers. The electrical pulse time duration can be from 0.1-2 msec. For layer resistivities as noted, energies of approximately 0.05-05J/cm² will provide the changes in the resistive layer that are necessary for localised imaging.

A recording medium has been described above in which a resistive layer has its properties locally changed in response to electrical currents from a multi-stylus recording head of the type used in resistive ribbon printing or electroerosion printing. Rather than requiring the erosion of a conductive layer or the transfer of an adjacent fusible ink layer, this type of recording medium is very efficient, because the electrical energy is converted to thermal energy in the layer in which the change is to occur. The resolution and print quality obtainable in resistive ribbon printing and electroerosion printing are also obtainable and can be exceeded with this type of recording medium, at power and energy levels less than that required for the prior art techniques.

Claims

1. A recording medium (10) for use in a recording apparatus comprising a substrate (12), a sensitive layer (16) and an electrically conducting layer (14),

characterised in that

said sensitive layer (16) is formed from a material which is hydrophilic at temperatures below about 150 degrees C and is capable of having its hydrophilicity locally reduced by the passage of electrical current therethrough.

2. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a polymer binder having conductive particles therein.

3. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a colour former which is activated at a temperature gr ater than about 200 degrees C.

4. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a polymer selected from the group consisting of hydrophilic polyamic acid having conductive particles therein, and silozane modified polyamic acid.

5. A recording medium as claimed in claim 4, characterised in that said polymer has thermally labile pendant groups on its polymer chain.

6. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises an ionic polymer.

7. A recording medium as claimed in claim 6, characterised in that said ionic polymer is a polyacrylic acid-polyamine complex.

8. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a polymer having conductive particles therein, said polymer being selected from the group consisting of low molecular weight Novolak-type resins and polyamines which undergo cross-linking upon the application of electrical current pulses of sufficient magnitude to produce enough resistive heating energy for said cross-linking.

9. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a polymer having conductive particles therein, said polymer being selected from the group consisting of high molecular weight polyamines, polyethers, polyoxyethylene aryl ether, polyvinylpyrrolidone, and polyvinyl acetal resins with thermal setting resins such as phenolics, epoxies, ureas, melamines and di-isocyanates.

10. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a polymer having conductive particles therein, said polymer being selected from the group consisting of polyfunctional monomers such as pentacrylthrital triacrylate as an additive in polyvinyl alcohol, polyacrylamide or polyacrylates, and diazopolyacrylamides which upon heating to a sufficient temperature will undergo the loss of a diazo group and cross-linking.

11. A recording medium as claimed in claim 1, characterised in that said sensitive layer comprises a polymer binder having conductive particles therein, the binder being selected from the group comprising cellulose acetate butyrate (CAB), CAB-urethane, epoxies, polyimides, polyorganosiloxanes and polyether-ur thane blends, polyacrylates such

as PMMA, glycidylmethacrylate, PFFA-resins, and polyvinyl alcohol-diazoacrylamides.

12. A recording apparatus including a recording medium (10) comprising a substrate (12), a sensitive layer (16) and an electrically conducting layer (14), and a recording head (18) for providing patterns of electrical current through selected regions of said sensitive layer

characterised in that

said sensitive layer (16) is formed from a material which is hydrophilic at temperatures below about 150 degrees C and is capabl of having its hydrophilicity locally reduced by the passage of electrical current therethrough,

and in that said electrical current is sufficiently strong to change said selected regions of said sensitive layer from hydrophilic to oleophilic.

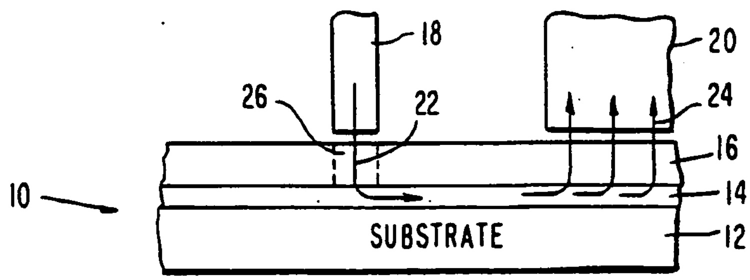

18
20
26
22
24
16
10
14
SUBSTRATE
12

FIG. 1

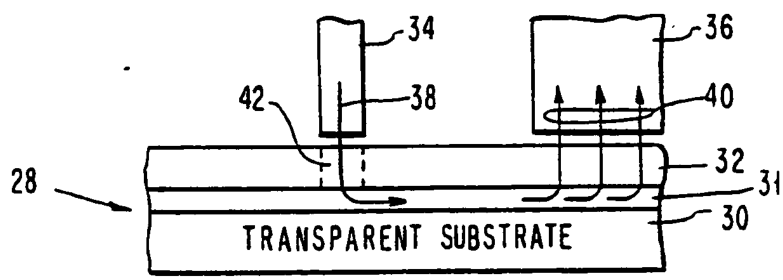

34
36
42
38
40
32
28
31
TRANSPARENT SUBSTRATE
30

FIG. 2

THERMAL RING CLOSURE OF A POLYIMIDE PRECURSOR:

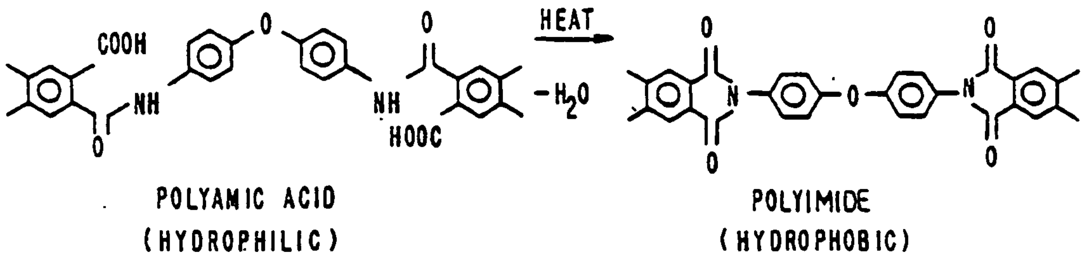


FIG 3

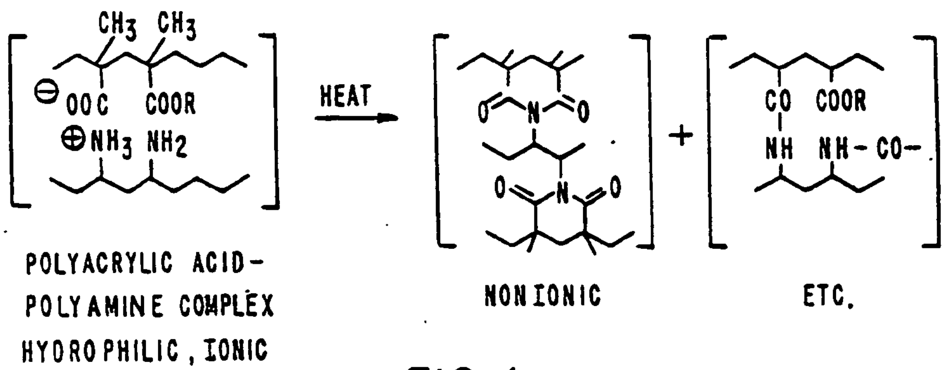


FIG. 4

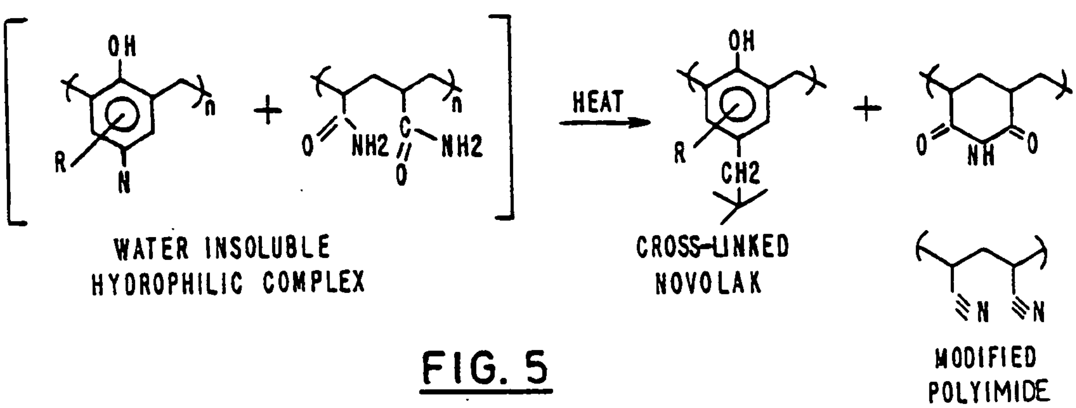
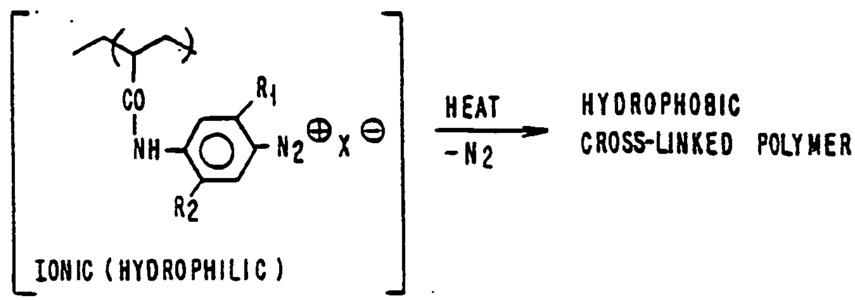
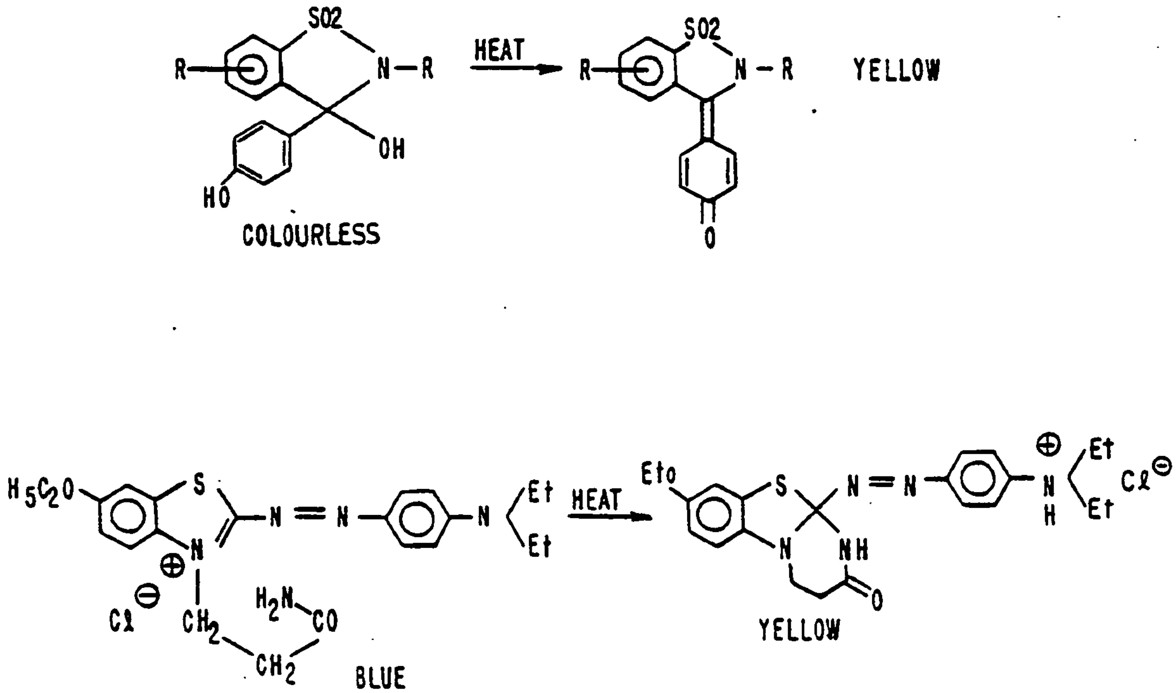


FIG. 5



HEAT
$-N_2$
HYDROPHOBIC CROSS-LINKED POLYMER
IONIC (HYDROPHILIC)

FIG. 6



HEAT
YELLOW
COLOURLESS
HEAT
YELLOW
BLUE

FIG. 7